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ANOMALOUS VARIATIONS OF THE INTENSITY OF SAMARIUM

SPECTRUM LINES IN A D. C. ARC
-USSR-

by R. R. Shvngiradze

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ANOMALOUS VARIATIONS OF THE INTENSITY OF SAMARIUM
SPECTRUM LINES IN A D. C. ARC

- USSR -

Following is a translation of an article by R. R. Shvengiradze in *Optika i Spektroskopiya* (Optics and Spectroscopy), Vol. V, No. 1, Moscow/Leningrad, July 1958, pages 88-90.

The similarity of chemical properties and a number of physical properties of the rare-earth (R. E.) elements and a majority of their compounds, which creates serious difficulties in chemical processes of separation, is favorable for spectral analysis.

The absence of selective evaporation and the arising of spectra of components of the mixture provides a high accuracy of analysis, even in those cases, when the source of the arising of the spectrum is characterized by high instability of electrical parameters, for example, in the case of a D. C. arc. This case has been repeatedly mentioned in the literature (1-5). However, some anomalies, observed under specific conditions, do not permit the application of this hypothesis to all the rare-earth elements (6).

In the present report are cited the results of the anomalous variations of the intensities of samarium spectrum lines, which has been observed.

Mixtures of oxides of rare-earth elements were mixed with graphite powder in the proportion 1:1 and were burned in the arc between carbon electrodes with a current power, equal to 5A. Spectrograph ISP-51 and camera UF-84 were used.

In figure 1, are represented curves, which indicate variations of blackening of spectrum lines of various rare-earth elements in the process of burning the arc every 15 sec. As is seen from the diagram, the intensity of the samarium spectrum lines varies differently, than the intensity of other rare-earth elements of the mixture which was investigated. As a result of this, the relative intensity of those pairs of lines, in which one of the lines belongs to samarium, substantially varies during the process of burning of the arc. The relative intensities of such pairs in relation to the time of burning of the arc are presented in fig. 1. On the other hand, the relative intensity of those pairs of lines, in which the lines of samarium are not involved, remains practically constant during the whole time of the burning of the arc, (curves, fig 1, B).

Upon the burning in the arc of a concentrate of samarium with low concentrations of admixtures of other rare-earth elements (0.02-0.1%) to the moment of total combustion of the sample, when the intensity of the spectrum of samarium begins to decrease, the intensity of the lines of the admixtures, sharply increases. This is seen from fig. 2, where are represented the variations of blackening S of the spectral lines in relation to the time of burning of the arc for this case. The observed phenomenon of a sharp increase of the intensities of the spectrum lines of the admixtures makes it possible in practice to raise the sensitivity of the discovery of admixtures in the surplus of samarium approximately for the order of magnitude. If other rare-earth elements, as for example Ce, Pr, Nd, La, Y, Dy are the main component of the investigated mixture, a similar phenomenon is not observed.

In fig. 3, a are represented curves of the relation of blackenings of lines of various rare-earth elements to the power of the current. From fig. 3 it is seen, that the intensity of the lines of samarium increases with an increase of the current of the arc up to a specific value (6A) and remains almost invariable with a further increase of the current. The intensity of the spectra of other rare-earth elements increases substantially within the investigated limits of the power of the current. Therefore the ratio of the intensities of those pairs of lines, in which one of the lines belongs to samarium, changes very substantially in relation to the power of the current (see curves in fig. 3), whereas the relative intensity of the pairs without the involvement of samarium lines changes insignificantly (curves in fig., 3B).

Observations on the variation of the relative intensities of homologous and non-homologous pairs of lines make it possible to come to the conclusion, that the cause of the anomalous behavior of samarium is not contained in the processes, which proceed in a gaseous cloud of the arc. Actually, in fig. 1, for the same elements are represented two pairs of lines, some of which are distinguished little, and the others are distinguished substantially for excitation energies. Inspite of this, in the behavior of these pairs there is almost not any difference (the values of the excitation energies are presented alongside of the values of the wave lengths). In 3,B is represented the variation of the ratio of the intensities of the two lines of samarium in respect to the power of the current. This ratio does not change at all, inspite of the fact, that the lines according to excitation energies differ from one another more substantially (by 0.6 v), than in the case of any other pairs (for this group in fig. 3 are presented only the excitation energies of the lines, which were investigated), consequently, the fluctuations in the gaseous cloud of the arc cannot be the cause of the anomalous behavior of samarium. It is contained in the processes of the transition of the substance from the solid state into the gaseous cloud of the arc. In the crater of the anode samarium undergoes other chemical transformations, than the other rare-earth elements. The tension of the vapors of the compound, in which samarium enters into the gaseous cloud, is greater, than the compound, in the form of which the other rare-earth elements

volatilize. Such a hypothesis is substantiated by the fact, that in the activated arc of alternating current between the copper electrodes with a baked sample in the crater of the electrode, the mentioned anomalies of samarium are not observed, because in the given case the character of the vaporization of the sample is somewhat different.

The following conclusions have a specific significance for practical work.

1. The use of samarium as an element of comparison upon spectral analysis of mixtures of rare-earth elements substantially reduce the accuracy of analysis.

2. On the basis of selective vaporization of samarium it is possible to increase significantly the sensitivity of the detection of admixtures in the concentrate of samarium.

3. The sensitivity of the spectral discovery of admixtures in samarium will be greater with high values of the power of the current of the arc; and the sensitivity of the spectral discovery of samarium in other rare elements will be greater with low values of the power of the current of the arc.

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31 December 1957

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FIGURE APPENDIX

Figure 1. Curves of blackening and the relative intensities of the pairs of lines in relation to the time of burning of the arc.

A. curves of blackening of the lines
 5 - relative intensities of the pairs of lines

1 -	Nd 4400.8	2.88
2 -	Sm 4205.1	3.05
3 -	Od 4217.1	3.22
4 -	Sm 4232.2	3.24
5 -	Nd 4196.8	2.88
6 -	Sm 4236.7	3.05
7 -	Pr 4141.3	3.54
8 -	Sm 4286.7	3.00
9 -	Od 4327.1	2.84
10 -	Sm 4286.7	3.08
11 -	Pr 4161.3	3.54
12 -	Sm 4265.1	3.02

B. relative intensities of pairs of lines (without Sm).

1 -	Nd 4272.8	2 -	Od 4238.8
2 -	La 4238.8	3 -	La 4336.4
3 -	Pr 4495.4	4 -	Od 4191.0
5 -	Nd 4686.4	6 -	Pr 4495.4
6 -	La 3988.4	7 -	Y 4682.3
7 -	Nd 4611.8	8 -	Na 4686.7
8 -	La 3995.8	9 -	La 4122.4
9 -	Nd 4018.8	10 -	Pr 6141.3

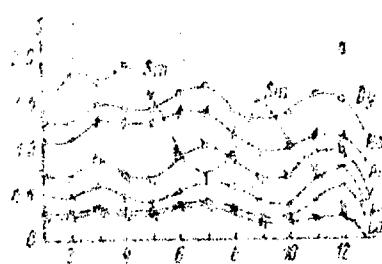
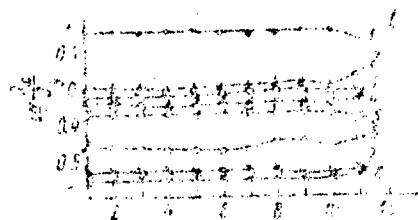


Figure 1. Successive expositions every 15 sec.



Successive expositions every 15 sec.



Successive expositions every 15 sec.

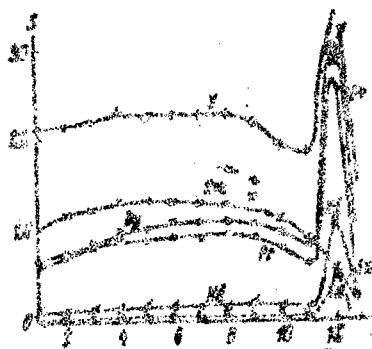


Figure 2. Successive expositions every 15 sec.
Curves of blackening of the spectrum lines in relation to the time of combustion of the concentrate of samarium in the arc.

Figure 3. Curves of blackening of the lines and the relative intensities of the pairs of lines in the spectra of rare earths in relation to the power of the current.
A. Curves of blackening of the lines
5 - relative intensities of the pairs of lines.

$$\begin{aligned}
 1 &= \frac{La 5964.8}{Sm 5986.1} ; \quad 2 = \frac{Nd 4277.3}{Sm 4287.7} ; \\
 3 &= \frac{Gd 4341.3}{Sm 4292.2} ; \quad 4 = \frac{Gd 4361.9}{Sm 4318.3} ; \\
 6 &= \frac{La 4238.4}{Sm 4287.7}
 \end{aligned}$$

$$\begin{aligned}
 1 &= \frac{Sm 3.4}{Sm 3.6} ; \quad 2 = \frac{Gd 3.2}{Gd 3.7} ; \\
 3 &= \frac{Pr 3.3}{Nd 3.5} ; \quad 4 = \frac{La 3.4}{Gd 3.3} ; \\
 5 &= \frac{Dy 3.2}{Nd 3.0} ; \quad 6 = \frac{La 3.4}{Nd 3.0} ; \\
 7 &= \frac{La 3.3}{Pr 3.3} ; \quad 8 = \frac{La 3.3}{Gd 3.7} .
 \end{aligned}$$

B. relative intensities of pairs of lines (without Sm)



Figure 3a. Power of Current (5A)

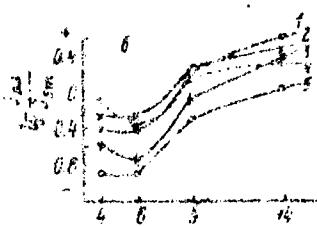


Figure 3. Power of Current (6A)

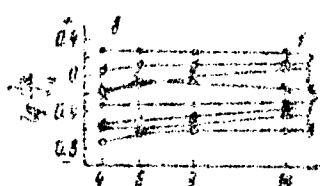


Figure 3B. Power of current (7A)